

Production of polyurethane foams

- The present invention relates to a process for producing
- 5 polyurethane foams by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries and also to the use of  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,
- 10  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in polyurethane foams.

- The production of polyisocyanate polyaddition products, for example polyurethanes which may contain urea and/or isocyanurate
- 15 structures, by reacting polyisocyanates with compounds which are reactive toward isocyanates in the presence of catalysts which accelerate the reaction of the isocyanate-reactive substances with isocyanates and in the presence or absence of blowing agents, additives and/or auxiliaries is generally known.
- 20 Like other synthetic polymers, polyisocyanate polyaddition products are subjected to ageing processes which generally lead to impairment of the use properties as time goes on. Significant ageing influences are, for example, hydrolysis, photooxidation
- 25 and thermooxidation which lead to rupture of bonds in the polymer chains. In the case of polyisocyanate polyaddition products, for example polyurethanes, hereinafter also referred to as PURs, the action of moisture and even more the combination of moisture and elevated temperature results in hydrolytic cleavage of the
- 30 urethane and urea bonds.

- This cleavage not only leads to a significant deterioration in the use properties but also leads to formation of aromatic amines such as toluenediamine (TDA) and diaminodiphenylmethane (MDA) or
- 35 aliphatic amines such as hexamethylenediamine or isophoronediamine.

- As experiments have shown, the amine formation is influenced by a series of parameters. In particular, high temperatures above 80°C
- 40 in combination with high atmospheric humidity lead to hydrolytic cleavage of the urethane and urea bonds. Such conditions are important in some specific application areas for flexible PUR foams.

- 45 A further parameter which has a significant influence on the formation of primary amines is the type and amount of catalysts used. As has been confirmed in various experiments, the catalysts

which are present in polyurethane systems and are necessary for the urethane formation and blowing reactions also catalyze the hydrolytic backdissociation reaction to a considerable extent. The presence of catalysts is thus a quite decisive prerequisite for the hydrolysis of the urethane and urea bonds. Furthermore, it has been able to be shown that the efficiency of the hydrolysis is highly dependent on the activity and type of catalyst and also on whether the catalyst remains in the system or can migrate out of the material. Especially tertiary amine catalysts containing reactive functional groups such as OH and NH<sub>2</sub> considerably accelerate amine formation by lowering the activation energy for the cleavage reaction. The functional groups result in incorporation of the catalysts into the PUR network formed and the products produced in this way have the advantage of lower odor and fogging problems since the catalysts cannot escape by diffusion after manufacture of the PUR products. The same applies to formulations comprising polyols which have been prepared using primary or secondary amines as initiator molecules and are thus catalytically active in the foam. Such foams have been increasingly used in recent times. In the case of formulations which comprise such constituents and in specific applications are exposed to particularly hot and humid conditions, the formation of primary amines as dissociation products cannot be ruled out. In contrast, in the case of foams containing amine catalysts having no functional groups which can be built into the foam, the catalysts are generally given off from the foam within a short time of manufacture or during the ageing of the foam. In the case of such foams, hot and humid conditions lead to significantly lower amine contents.

In order to reduce the occurrence of primary amines specifically in the case of PUR products which are exposed to hot and humid conditions, it was necessary to find additives which react with primary amine dissociation products to form chemically more acceptable compounds. These additives should not significantly influence the foaming reaction.

As compounds which reduce the content of primary aromatic amines in flexible polyurethane foams, stearically hindered cycloaliphatic monoisocyanates and monothioisocyanates are used according to US 4211847, GB 1565124 and DE-A 2946625. Owing to their stearic hindrance and their lower reactivity compared to aromatic isocyanates, these isocyanates react to only a small extent during the foaming reaction, so that free isocyanate is available after the foaming reaction is complete to react with any aromatic amines present. Disadvantages of these known teachings are that the compounds specified are relatively

expensive and that especially the two last-named compounds participate to at least some extent in the urethane formation reaction despite their steric hindrance and do not only react with aromatic amine formed after the foaming reaction. In addition, these isocyanates tend, owing to their low vapor pressure, to migrate out of the finished foam and thus represent a further health hazard due to the release of free isocyanate.

US 5821292 describes 3-arylacrylic esters as light stabilizers, oxidation inhibitors and heat stabilizers for organic polymers. This document does not discuss an improvement in the hydrolytic stability and especially a reaction with primary aromatic and aliphatic amines.

DE-A 42 32 420 discloses the use of  $\alpha,\beta$ -unsaturated ester carboxylates for producing polyurethane foams which have an improved compressive strength and elongation at break. In this document, salts of  $\alpha,\beta$ -unsaturated ester carboxylates are used as catalysts for the NCO/water reaction. In a subordinate clause, it is stated that the compounds are, owing to the presence of olefinic double bonds in the vicinity of the carboxylate groups, capable of addition onto amino groups which are formed during the slow ageing of the foam. A disadvantage of these compounds is their catalytic action which has an adverse effect on the foaming reaction. A catalytic action of additives to reduce the amine contents in finished PUR foams is undesirable since, as described above, it leads to further and accelerated formation of primary amines.

It is an object of the present invention to develop a process for producing polyurethane foams, which may include isocyanurate and/or urea structures, preferably flexible polyurethane foams, by reacting isocyanates with compounds which are reactive toward isocyanates in the presence of blowing agents and in the presence or absence of catalysts, additives and/or auxiliaries, which process makes it possible to decrease the content of, in particular, primary amines formed by hydrolytic cleavage of urethane and urea bonds by chemical reaction. In particular, additives which are able to reduce the content of primary, preferably primary aromatic, amines in flexible PUR foams are to be found. The amine traps should as far as possible be inexpensive and readily available and should act in the finished foam without further after-treatment. The compounds (i) should preferably have a vapor pressure which is not too low in order to avoid migration from the foam.

We have found that this object is achieved by carrying out the reaction in the presence of at least one of the following compounds (i): an  $\alpha,\beta$ -unsaturated carboxylic acid, an  $\alpha,\beta$ -unsaturated carboxylic acid derivative, an  $\alpha,\beta$ -unsaturated ketone and/or an  $\alpha,\beta$ -unsaturated aldehyde.

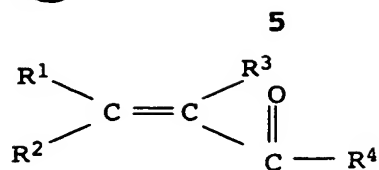
As a result of the use according to the present invention of compound (i), any free amino groups formed by undesired cleavage of urethane and/or urea bonds are bound by reaction with the novel compounds (i).

Both primary and secondary amines are capable of adding onto C=C double bonds, particularly when the latter are in the vicinity of a carbonyl group. The Michael addition of the amine occurs onto the unsaturated system in which the  $\pi$  electrons are delocalized over the carbonyl group. As has been established in experiments, temperatures of from 70 to 120°C, as can occur under hot and humid conditions, for example in steam sterilization or cleaning with hot steam, are surprisingly sufficient to react primary amine formed in the PUR foam by hydrolytic cleavage of urethane and urea bonds at least partly with the compounds (i) used according to the present invention.

The compounds (i) are thus employed in polyurethane foams to react with amino groups. The amino groups are bound by addition onto the C=C double bonds and to the  $\alpha,\beta$ -unsaturated carbonyl compounds used according to the present invention to form a covalent bond. The diffusion or migration of primary amines from the polyurethane foam can thus be reduced according to the present invention. This is particularly true if the compounds (i) are built into the polyurethane network formed due to the presence of groups which can be built in, e.g. OH or NH<sub>2</sub>. In this way, not only are the compounds (i) fixed and their diffusion from the polyurethane foam thus prevented, but the primary amine bound to the compound (i) is also fixed.

As (i), it is possible to use generally known  $\alpha,\beta$ -unsaturated carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes.

Preference is given to compounds (i) which include the following structural feature:



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where the radicals  $\text{R}^1$  to  $\text{R}^4$  have the following meanings:

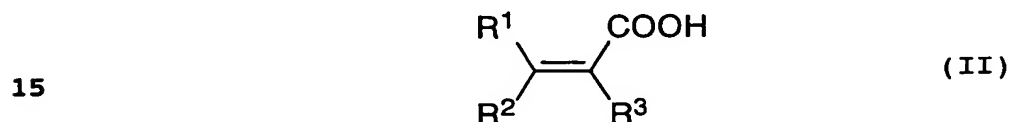
- $\text{R}^1$ : H,  $\text{C}_1$ - $\text{C}_{12}$ -alkyl,  $\text{C}_6$ - $\text{C}_{20}$ -aryl,  
 $\text{R}^2$ : H,  $\text{C}_1$ - $\text{C}_{12}$ -alkyl,  $\text{C}_6$ - $\text{C}_{20}$ -aryl,  
 10  $\text{R}^3$ : H,  $\text{C}_1$ - $\text{C}_{12}$ -alkyl,  $\text{C}_6$ - $\text{C}_{20}$ -aryl,  
 $\text{R}^4$ : H,  $\text{C}_1$ - $\text{C}_{12}$ -alkyl,  $\text{C}_6$ - $\text{C}_{20}$ -aryl,  $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl,  
 $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl-OH,  $-\text{C}_1$ - $\text{C}_{12}$ -alkyl-OH,  $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl,  
 $-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{NH}_2$ ,  $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{NH}_2$ ,  $-\text{O}$ -benzyl,  $-\text{O}$ -aryl,  
 $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{COOH}$ ,  $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{CH}(\text{OH})-\text{CH}_2-\text{O}-(\text{CO})-\text{CHCH}_2$ ,  
 15  $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{O}-(\text{CO})-\text{CHCH}_2$ ,  $-\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{CH}(\text{OH})-\text{C}_1$ - $\text{C}_{12}$ -  
 alkyl- $\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{O}-\text{C}_1$ - $\text{C}_{12}$ -alkyl- $\text{CH}(\text{OH})-\text{CH}_2-\text{O}-(\text{CO})-\text{CHCH}_2$ .

- Particular preference is given to the following compounds as (i): acrylic acid, crotonic acid, isocrotonic acid, sorbic acid,
- 20 fumaric acid, cinnamic acid, hydroxyethyl acrylate, 3-acryloyloxy-2-hydroxypropyl methacrylate, benzyl cinnamate, trans-3-nonen-2-one, benzalacetone, dibenzalacetone, benzalacetophenone, 1-methylbenzalacetophenone, crotonaldehyde, cinnamaldehyde, methyl vinyl ketone and/or  $\alpha, \beta$ -unsaturated
- 25 polyester diols prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid and/or acrylic acid with oligomeric diols such as butanediol, diethylene glycol, propylene glycol or 1,3-propanediol and/or triols such as glycerol and having a molecular weight factor per double bond of from 150 to
- 30 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.

- Very particular preference is given to using the following compounds as (i): hydroxyethyl acrylate,
- 35 3-acryloyloxy-2-hydroxypropyl methacrylate, trans-3-nonen-2-one, benzyl cinnamate, crotonic acid and/or  $\alpha, \beta$ -unsaturated polyester diols (A) prepared by polycondensation of maleic acid, fumaric acid, methacrylic acid or acrylic acid with oligomeric diols such as butanediol, diethylene glycol, propylene glycol or
- 40 1,3-propanediol and/or triols such as glycerol and having a molecular weight factor per double bond of from 150 to 3000, a functionality of from 2 to 6, a hydroxyl number of from 20 to 800 and an acid number of from 0 to 15.
- 45 Besides a pure polycondensation of an  $\alpha, \beta$ -unsaturated carboxylic acid, preferably dicarboxylic acid, with diols and/or triols, the  $\alpha, \beta$ -unsaturated polyester diols (A) can be prepared, for example,

- by reaction of a polyhydric alcohol (B) with a compound (C) containing an epoxy function and additionally a functional group which is reactive toward alcohols to give a compound (D) and reaction of this compound (D) with an  $\alpha,\beta$ -olefinically
- 5 unsaturated carboxylic acid (E) to form the compound (A) used according to the present invention or by direct reaction of an  $\alpha,\beta$ -olefinically unsaturated carboxylic acid (E) with (B) to give a compound (A). Suitable compounds (B) are polyhydric, in particular dihydric, alcohols. Use can advantageously be made of
- 10 alcohols having from 2 to 30, preferably from 2 to 20, carbon atoms, e.g. diols such as 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-hexanediol, 1,8-octanediol, 1,10-decanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol,
- 15 2-methyl-2-butyl-1,3-propanediol, 2,2-dimethyl-1,4-butanediol, 2,3-dimethyl-2,3-butanediol, 2-butene-1,4-diol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,3-cyclohexanediol, menthol, 1,4-cyclohexanedimethanol, neopentyl glycol, hydroxypivalate, diethylene glycol, triethylene glycol,
- 20 tetraethylene glycol, dipropylene glycol or methyldiethanolamine and triols such as glycerol, trimethylolpropane or 1,2,4-butanetriol and alcohols having at least four hydroxy groups, e.g. pentaerythritol, sorbitol, threitol, mannitol or dulcitol or aromatic-aliphatic or aromatic-cycloaliphatic diols
- 25 having from 8 to 30 carbon atoms, where possible aromatic structures are heterocyclic ring systems or preferably isocyclic ring systems such as naphthalene or in particular benzene derivatives, e.g. hydroquinone, 4,4'-dihydroxybiphenyl, bisphenol A, symmetrically diethoxylated bisphenol A, symmetrically
- 30 dipropoxylated bisphenol A, higher ethoxylated or propoxylated bisphenol A derivatives or bisphenol F derivatives, commercial polyetherols such as Lupranol<sup>®</sup>, Pluracol<sup>®</sup> (BASF), Systol<sup>®</sup> (BASF), Baycoll<sup>®</sup> (Bayer), Caradol<sup>®</sup> (Shell), Arcol<sup>®</sup> (Lyondell), Varanol<sup>®</sup> (DOW Chemical), Polypol<sup>®</sup> (Polioles), Teracol<sup>®</sup> (Enichem), and also
- 35 mixtures of such compounds. As compounds (C) which react with the hydroxyl groups of (B), it is possible to use many classes of substances, e.g. epoxidated olefins, glycidyl esters of saturated or unsaturated carboxylic acids, glycidyl ethers of aliphatic or aromatic polyols or epoxyalkyl halides. Examples of suitable
- 40 compounds are (+)-1-chloro-2,3-epoxy-2-methyl-propane, (-)-1-chloro-2,3-epoxy-2-methylpropane, (1)-chloro-2,3-epoxy-2-methyl-propane, in particular (+)-1-chloro-2,3-epoxypropane, (-)-1-chloro-2,3-epoxypropane or (1)-chloro-2,3-epoxypropane, and also mixtures of such compounds.
- 45 The reaction to form the compound (D) used according to the present invention can be carried out in a manner known per se, as described, for example, in C.A. May, Epoxy Resins Chemistry and

Technology, Marcel Dekker Inc., New York/Basle, 1988. Such compounds are known per se. Particular preference is given to polyglycidyl compounds of the bisphenol A type and glycidyl ethers of polyfunctional alcohols, e.g. of butanediol, of  
 5 hexanediol, of neopentyl glycol, of 1,4-cyclohexanedimethanol, of glycerol and of pentaerythritol, for example Epikote 812, Epikote 828 and Epikote 162 from Shell or Heloxy 68 and Heloxy 107 from Rhône-Poulenc. The compound (D) can be isolated from the reaction mixture by known methods, e.g. by extraction, precipitation or  
 10 spray drying, and advantageously used for preparing the compound (A). Suitable compounds (E) are first and foremost carboxylic acids of the formula (II)



where R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are hydrogen or C<sub>1</sub>-C<sub>4</sub>-alkyl radicals; preference is given to maleic acid, fumaric acid, acrylic acid  
 20 and methacrylic acid. It is also possible to use mixtures of various carboxylic acids of this type.

The reaction to form the compound (A) used according to the present invention can be carried out in a manner known per se,  
 25 preferably at from 90 to 130°C, particularly preferably from 100 to 110°C, and advantageously until the reaction mixture has an acid number of less than 5 mg KOH/g.

Particular preference is given to the reaction of (B) with (E) to  
 30 give the compound (A) used according to the present invention.

As catalysts for the reaction of a compound (D) with a compound (E), it is possible to use, for example, KOH, quaternary ammonium or phosphonium compounds, tertiary amines, phosphines such as  
 35 triphenylphosphine or Lewis bases such as thiodiglycol.

The catalysts are preferably used in amounts of from 0.01 to 5% by weight, particularly preferably from 0.1 to 3% by weight, based on the compound (D).

40 The use of a solvent or diluent is not necessary, but is preferred.

Suitable solvents or diluents are hydrocarbons, in particular  
 45 toluene, xylene or cyclohexane, esters, in particular ethyl glycol acetate, ethyl acetate or butyl acetate, amides, in particular dimethylformamide or N-methylpyrrolidone, sulfoxides,

in particular dimethyl sulfoxide, ketones, in particular methyl ethyl ketone or cyclohexanone, ethers, in particular diisopropyl ether or methyl tert-butyl ether, or preferably cyclic ethers, in particular tetrahydrofuran or dioxane. The solvents or diluents 5 can be used individually or as a mixture.

To avoid premature polymerization, the reaction, particularly with acrylic acid or methacrylic acid, is advantageously carried out in the presence of small amounts of inhibitors. Possible 10 inhibitors are the customary compounds used for preventing thermal polymerization, e.g. hydroquinone, hydroquinone monoalkyl ethers, 2,6-di-tert-butylphenol, N-nitrosamines of phenothiazines or phosphorous esters. They are generally used in amounts of from 0.005 to 0.5% by weight, based on the compound (E).

15 The compound (A) can be isolated from the reaction mixture by known methods, e.g. by extraction, precipitation, drying or spray drying.

20 As mentioned above,  $\alpha,\beta$ -unsaturated carbonyl compounds having additional functional groups such as OH and  $\text{NH}_2$  which are built into the PUR network lead to a particularly significant reduction in the MDA and TDA contents. Examples which may be mentioned are hydroxyethyl acrylate and 3-acryloyloxy-2-hydroxypropyl 25 methacrylate. Polyols having integrated C=C double bonds conjugated with the carbonyl group have a similar action.

Particular preference is generally given to compounds (i) which dissolve readily in the isocyanates or the compounds which are 30 reactive toward isocyanates. Preference is given to using (i) in admixture with the isocyanates.

In the process of the present invention for producing polyurethane foams, (i) is preferably used in an amount of from 35 0.1 to 20% by weight, particularly preferably from 0.5 to 10% by weight, based on the weight of the polyurethane foam.

The polyurethane foams obtainable according to the present invention have the particular advantage that any primary amines 40 formed by hydrolysis, in particular primary aromatic amines, are converted by the compounds (i) into an unproblematical form. The polyurethane foams, in particular mattresses, furniture upholstery or foam backing of carpets, thus particularly preferably comprise products of the reaction of primary and/or 45 secondary amines, preferably aromatic amines, with the abovementioned compounds (i), i.e. the  $\alpha,\beta$ -unsaturated carboxylic

acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  
 $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes.

Preference is accordingly given to the use of  $\alpha,\beta$ -unsaturated  
5 carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  
 $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in  
polyurethane foams having a reduced primary amine content, in  
particular by reaction of the compounds (i) with the amino groups  
in the polyurethane foams, i.e. the use of  $\alpha,\beta$ -unsaturated  
10 carboxylic acids,  $\alpha,\beta$ -unsaturated carboxylic acid derivatives,  
 $\alpha,\beta$ -unsaturated ketones and/or  $\alpha,\beta$ -unsaturated aldehydes in  
polyurethane foams to react with primary amines.

As isocyanates to be used in the process for producing  
15 polyurethane foams, it is possible to use, for example, the  
compounds described below:

Isocyanates which can be used are the aliphatic, cycloaliphatic,  
araliphatic and preferably aromatic organic isocyanates known per  
20 se, preferably polyfunctional isocyanates, particularly  
preferably diisocyanates.

Specific examples are: alkylene diisocyanates having from 4 to 12  
carbon atoms in the alkylene radical, e.g. dodecane  
25 1,12-diisocyanate, 2-ethyltetramethylene 1,4-diisocyanate,  
2-methylpentamethylene 1,5-diisocyanate, tetramethylene  
1,4-diisocyanate and preferably hexamethylene 1,6-diisocyanate;  
cycloaliphatic diisocyanates such as cyclohexane 1,3- and  
1,4-diisocyanate and also any mixtures of these isomers,  
30 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane  
(isophorone diisocyanate), hexahydrotolylene 2,4- and  
2,6-diisocyanate and also the corresponding isomer mixtures,  
dicyclohexylmethane 4,4'-, 2,2'- and 2,4'-diisocyanate and also  
the corresponding isomer mixtures, aromatic diisocyanates and  
35 polyisocyanates such as tolylene 2,4- and 2,6-diisocyanate (TDI)  
and the corresponding isomer mixtures, diphenylmethane 4,4'-,  
2,4'- and 2,2'-diisocyanate (MDI) and the corresponding isomer  
mixtures, naphthalene 1,5-diisocyanate (NDI), mixtures of  
diphenylmethane 4,4'- and 2,4'-diisocyanates, mixtures of NDI and  
40 diphenylmethane 4,4'- and/or 2,4'-diisocyanates,  
3,3'-dimethyl-4,4'-diisocyanatobiphenyl (TODI), mixtures of TODI  
and diphenylmethane 4,4'- and/or 2,4'-diisocyanates,  
polyphenylpolymethylene polyisocyanates, mixtures of  
diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanates and  
45 polyphenylpolymethylene polyisocyanates (crude MDI) and mixtures  
of crude MDI and tolylene diisocyanates. The organic

diisocyanates and polyisocyanates can be used individually or in the form of their mixtures.

Use is frequently also made of modified polyfunctional

- 5 isocyanates, i.e. products which are obtained by chemical reaction of organic diisocyanates and/or polyisocyanates. Examples which may be mentioned are diisocyanates and/or polyisocyanates containing ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione and/or urethane groups.
- 10 Specific examples are: organic, preferably aromatic polyisocyanates containing urethane groups and having NCO contents of from 33.6 to 15% by weight, preferably from 31 to 21% by weight, based on the total weight, modified diphenylmethane 4,4'-diisocyanate, modified diphenylmethane 4,4'- and
- 15 2,4'-diisocyanate mixtures, modified NDI, modified TODI, modified crude MDI and/or tolylene 2,4- or 2,6-diisocyanate, with examples of dialkylene and polyoxyalkylene glycols which can be used individually or as mixtures being: diethylene glycol, dipropylene glycol, polyoxyethylene, polyoxypropylene and
- 20 polyoxypropylene-polyoxyethylene glycols, triols and/or tetrols. Further suitable modified isocyanates are prepolymers containing NCO groups, having NCO contents of from 25 to 3.5% by weight, preferably from 21 to 14% by weight, based on the total weight, and prepared from, for example, polyester polyols and/or
- 25 preferably polyether polyols and diphenylmethane 4,4'-diisocyanate, mixtures of diphenylmethane 2,4'- and 4,4'-diisocyanate, NDI, TODI, mixtures of NDI and isomers of MDI, tolylene 2,4- and/or 2,6-diisocyanates or crude MDI. Other modified isocyanates which have been found to be useful are
- 30 liquid polyisocyanates containing carbodiimide groups and/or isocyanurate rings and having NCO contents of from 33.6 to 15% by weight, preferably from 31 to 21% by weight, based on the total weight, e.g. those based on diphenylmethane 4,4'-, 2,4'- and/or 2,2'-diisocyanate, NDI, TODI and/or tolylene 2,4- and/or
- 35 2,6-diisocyanate.

The modified polyisocyanates can, if desired, be mixed with one another or with unmodified organic polyisocyanates such as diphenylmethane 2,4'- and/or 4,4'-diisocyanate, NDI, TODI, crude

- 40 MDI, tolylene 2,4- and/or 2,6-diisocyanate.

As isocyanates in the mixtures or process according to the present invention, preference is given to using diphenylmethane 4,4'-, 2,4'- and/or 2,2'-diisocyanate, tolylene 2,4- and/or

- 45 2,6-diisocyanate, NDI, hexamethylene diisocyanate and/or

isophorone diisocyanate; these isocyanates can be used both in any mixtures and in modified form as described above.

As compounds which are reactive toward isocyanates and usually have at least two reactive hydrogen atoms, customarily hydroxyl and/or amino groups, use is advantageously made of ones having a functionality of from 2 to 8, preferably from 2 to 6, and a molecular weight of usually from 60 to 10,000. Compounds which have been found to be useful are, for example, polyether  
10 polyamines and/or preferably polyols selected from the group consisting of polyether polyols, polyester polyols, polythioether polyols, polyesteramides, hydroxyl-containing polyacetals and hydroxyl-containing aliphatic polycarbonates or mixtures of at least two of the polyols mentioned. Preference is given to using  
15 polyester polyols and/or polyether polyols which can be prepared by known methods.

The polyester polyols preferably have a functionality of from 2 to 4, in particular from 2 to 3, and a molecular weight of  
20 usually from 500 to 3000, preferably from 1200 to 3000 and in particular from 1800 to 2500.

The polyether polyols have a functionality of preferably from 2 to 6 and usually have molecular weights of from 500 to 8000.  
25 Suitable polyether polyols also include, for example, polymer-modified polyether polyols, preferably graft polyether polyols, particularly those based on styrene and/or acrylonitrile which can be prepared by in-situ polymerization of acrylonitrile,  
30 styrene or preferably mixtures of styrene and acrylonitrile.

Like the polyester polyols, the polyether polyols can be used individually or in the form of mixtures. They can also be mixed with the graft polyether polyols or polyester polyols and with  
35 hydroxyl-containing polyesteramides, polyacetals and/or polycarbonates.

Polyol components used for rigid polyurethane foams, which may, if desired, contain isocyanurate structures, are  
40 high-functionality polyols, in particular polyether polyols based on high-functionality alcohols, sugar alcohols and/or saccharides as initiator molecules while polyol components used for flexible foams are 2- and/or 3-functional polyether polyols and/or polyester polyols based on glycerol and/or trimethylolpropane  
45 and/or glycols as initiator molecules or alcohols to be esterified. The polyether polyols are prepared by known techniques. Examples of alkylene oxides which are suitable for

preparing the polyols are tetrahydrofuran, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, styrene oxide and preferably ethylene oxide and 1,2-propylene oxide. The alkylene oxides can be used individually, alternately in succession or as mixtures.

- 5 Preference is given to using alkylene oxides which lead to primary hydroxyl groups in the polyol. Particularly preferred polyols are those which have been alkoxyated with ethylene oxide at the end of the alkoxylation and thus have primary hydroxyl groups. To produce thermoplastic polyurethanes, preference is  
10 given to using polyols having a functionality of from 2 to 2.2 and no crosslinkers.

- Furthermore, chain extenders and/or crosslinkers can be used as compounds which are reactive toward isocyanates. The addition of  
15 chain extenders, crosslinkers or, if desired, mixtures thereof can prove to be advantageous for, for example, modifying the mechanical properties, e.g. the hardness, of the polyisocyanate polyaddition products produced using these substances. As chain extenders and/or crosslinkers, it is possible to use water, diols  
20 and/or triols having molecular weights of from 60 to < 500, preferably from 60 to 300. Suitable chain extenders/crosslinkers are, for example, aliphatic, cycloaliphatic and/or araliphatic diols having from 2 to 14, preferably from 4 to 10, carbon atoms, e.g. ethylene glycol, 1,3-propanediol, 1,10-decanediol, o-, m-,  
25 p-dihydroxycyclohexane, diethylene glycol, dipropylene glycol and preferably 1,4-butanediol, 1,6-hexanediol and bis(2-hydroxyethyl)hydroquinone, triols such as 1,2,4- and/or 1,3,5-trihydroxycyclohexane, glycerol and trimethylolpropane and low molecular weight hydroxyl-containing polyalkylene oxides  
30 based on ethylene oxide and/or 1,2-propylene oxide and diols and/or triols as initiator molecules.

- If chain extenders, crosslinkers or mixtures thereof are employed for producing the polyisocyanate polyaddition products, they are  
35 advantageously used in an amount of from 0 to 20% by weight, preferably from 2 to 8% by weight, based on the weight of the compounds which are reactive toward isocyanates; thermoplastic polyurethanes are preferably produced without using crosslinkers.

- 40 For the purposes of the present invention, compounds which are reactive toward isocyanates are by definition considered only to include those which do not come under the definition of (i).

- Suitable catalysts are generally customary compounds, for example  
45 organic amines such as triethylamine, triethylenediamine, tributylamine, dimethylbenzylamine, N,N,N',N'-tetramethylethylenediamine,

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- N,N,N',N'-tetramethylbutanediamine,  
 N,N,N',N'-tetramethylhexane-1,6-diamine, dimethylcyclohexylamine,  
 pentamethyldipropylenetriamine, pentamethyldiethylenetriamine,  
 3-methyl-6-dimethylamino-3-azapentol, dimethylaminopropylamine,  
 5 1,3-bis(dimethylamino)butane, bis(2-dimethylaminoethyl) ether,  
 N-ethylmorpholine, N-methylmorpholine, N-cyclohexylmorpholine,  
 2-dimethylaminoethoxyethanol, dimethylethanolamine,  
 tetramethylhexamethylenediamine,  
 dimethylamino-N-methylethanolamine, N-methylimidazole,  
 10 N-(3-aminopropyl)imidazole, N-(3-aminopropyl)-2-methylimidazole,  
 1-(2-hydroxyethyl)imidazole,  
 N-formyl-N,N'-dimethylbutylenediamine,  
 N-dimethylaminoethylmorpholine,  
 3,3'-bis(dimethylamino)di-n-propylamine and/or  
 15 bis(2-piperazinoisopropyl) ether, dimethylpiperazine,  
 N,N'-bis(3-aminopropyl)ethylenediamine and/or  
 tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, or mixtures  
 comprising at least two of the abovementioned amines. It is also  
 possible to use relatively high molecular weight tertiary amines  
 20 as are described, for example, in DE-A 28 12 256. Further  
 catalysts which can be used are organic metal compounds customary  
 for this purpose, preferably organic tin compounds such as  
 tin(II) salts of organic carboxylic acids, e.g. tin(II) acetate,  
 tin(II) octoate, tin(II) ethylhexanoate and tin(II) laurate, and  
 25 the dialkyltin(IV) salts of organic carboxylic acids, e.g.  
 dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate  
 and dioctyltin diacetate. Tertiary aliphatic and/or  
 cycloaliphatic amines are preferably present in the mixtures;  
 triethylenediamine is particularly preferably present.  
 30  
 As blowing agents, it is possible to use, preferably for  
 producing foam polyurethanes, generally known blowing agents such  
 as materials which have a boiling point at atmospheric pressure  
 in the range from -40°C to 120°C, gases and/or solid blowing  
 35 agents and/or water in customary amounts, for example carbon  
 dioxide, alkanes and/or cycloalkanes such as isobutane, propane,  
 n- or iso-butane, n-pentane and cyclopentane, ethers such as  
 diethyl ether, methyl isobutyl ether and dimethyl ether,  
 nitrogen, oxygen, helium, argon, nitrous oxide, halogenated  
 40 hydrocarbons and/or partially halogenated hydrocarbons such as  
 trifluoromethane, monochlorotrifluoroethane, difluoroethane,  
 pentafluoroethane, tetrafluoroethane or mixtures comprising at  
 least two of the blowing agents mentioned by way of example.

As auxiliaries and/or additives, mention may be made of, for example, surface-active substances, foam stabilizers, cell regulators, fillers, dyes, pigments, flame retardants, hydrolysis inhibitors, fungistatic and bacteriostatic substances.

5

The starting materials for producing the polyurethane foams have been described above by way of example. The organic polyisocyanates and the compounds which are reactive toward isocyanates and have a molecular weight of from 60 to

10 10,000 g/mol are usually reacted in such amounts that the equivalence ratio of NCO groups of the polyisocyanates to the sum of the reactive hydrogen atoms of the compounds which are reactive toward isocyanates is 0.5-5:1, preferably 0.9-3:1 and in particular 0.95-2:1.

15

It may be advantageous for the polyurethanes to contain at least some bound isocyanurate groups. In these cases, a ratio of NCO groups of the polyisocyanates to the sum of the reactive hydrogen atoms of 1.5-60:1, preferably 1.5-8:1, is preferably selected.

20

The polyurethane foams can be produced, for example, by the one-shot method or by the known prepolymer method, for example with the aid of high-pressure or low-pressure technology in open or closed molds, reaction extruders or belt units.

25

It has been found to be advantageous to produce the polyurethane foams by the two-component process and to combine the compounds which are reactive toward isocyanates and, if appropriate, the catalysts, blowing agents and/or auxiliaries and/or additives as

30 the A component and to use the isocyanates and catalysts and/or blowing agents as B components.

The process of the present invention is preferably used for producing upholstery for furniture or automobiles, mattresses, in particular hospital mattresses, foam backing for carpets, PUR foams for backfoaming instrument panels or steering wheels or shoe soles.

35

The invention is illustrated by the following examples.

#### 40 Examples

To simulate conditions which can occur in the specific applications mentioned above, ageing under hot and humid conditions was carried out on samples of the flexible foams described below. For this purpose, test cubes of the foams to be tested having an edge length of 3 cm were in each case aged at

45

90°C and 90% relative atmospheric humidity for 72 hours in an air-conditioned chamber. Under these conditions, it is possible for hydrolytic cleavage of urethane and urea bonds to occur, resulting in formation of primary aromatic amines. The amine  
5 formed was subsequently extracted by means of a method developed by Prof. Skarping, University of Lund. For this purpose, the foam was squeezed out 10 times with 10 ml of acetic acid (w = 1% by weight). With the foam specimen compressed, the acetic acid was transferred to a 50 ml volumetric flask. The procedure was  
10 repeated twice and the volumetric flask was made up to the mark with acetic acid. The MDA/TDA content of the combined extracts was subsequently determined by means of capillary electrophoresis with UV detection. The MDA/TDA contents reported in the table correspond to the absolute contents of MDA/TDA formed in the PUR  
15 foam.

#### Example 1

Production of a flexible polyurethane foam by mixing 750 g of A  
20 component with 354 g of B component (index: 90) and transferring the foaming mixture into an aluminum mold (40 x 40 x 10 cm) heated to 53°C, with the components having the following compositions:

#### 25 A Component

97 parts of a polyol having a hydroxyl number (OHN) of 28 mg KOH/g, a mean functionality of 2.3 and an ethylene oxide (EO)/propylene oxide (PO) ratio of 14/86,  
30

3 parts of a polyol having an OHN of 42 mg KOH/g, a mean functionality of 3 and a PO/EO ratio of 30/70,

3.31 parts of water,

35 0.8 part of aminopropylimidazole,  
0.6 part of Lupragen® N 107, OHN: 421 (BASF Aktiengesellschaft),  
0.5 part of Tegostab B 8631 (Goldschmidt).

#### B component

40

Mixture of 50% of a polymeric MDI and 50% of a bifunctional MDI mixture.

As catalysts which can be built into the polyurethane, this  
45 system contains aminopropylimidazole and Lupragen® N 107 (BASF Aktiengesellschaft). It was selected to show the particular effectiveness of the additives in PUR formulations containing

catalysts which can be built into the polyurethane and catalytically active spacer polyols, as illustrated by the significant reduction of the MDA contents of foams with addition of  $\alpha,\beta$ -unsaturated carbonyl compounds compared to the comparative system in Table 1.

Table 1: Comparison of the MDA contents of flexible PUR foams without (foam 1) and with addition of  $\alpha,\beta$ -unsaturated carbonyl compounds (foams 2 to 8)

10

Foam	1	2	3	4	5	6	7	8
Hydroxyethyl acrylate [% by weight to (A)]	-	10	-	-	-	-	-	-
3-(Acryloyloxy)-2-hydroxy-propyl methacrylate	-	-	10	-	-	-	-	-
Laromer® 8765 [% by weight to A]	-	-	-	10	-	-	-	-
Lupragen® VP 9198 [% by weight to A]	-	-	-	-	10	-	-	-
trans-3-Nonen-2-one [% by weight to (A)]	-	-	-	-	-	9.6	-	-
Benzyl cinnamate [% by weight to (B)]	-	-	-	-	-	-	7.2	-
Crotonic anhydride [% by weight to (B)]	-	-	-	-	-	-	-	2
Cream time [s]	13	15	15	15	20	15	25	20
Gel time [s]	80	90	95	95	95	85	95	95
Rise time [s]	100	110	150	115	110	120	120	140
4,4'-MDA [ppm] w.o.a.	<1	<1	<1	<1	<1	<1	<1	<1
2,4'-MDA [ppm] w.o.a.	<1	<1	<1	<1	<1	<1	<1	<1
4,4'-MDA [ppm] w.a.	397	31	59	55	43	223	155	98
2,4'-MDA [ppm] w.a.	687	86	134	118	105	391	321	184

(A): Addition of (i) to the polyol component

(B): Addition of (i) to the isocyanate component

w.o.a.: Extraction after processing of the foam

w.a.: Extraction after hot-humid ageing for 3 days at 90°C and 90% relative atmospheric humidity in an air-conditioned chamber

Laromer® 8765 (BASF Aktiengesellschaft): OH-containing bisacrylic ester having a molecular weight of 346.4 g/mol and an OHN of 323 mg KOH/g.

Lupragen® VP 9198 (BASF Aktiengesellschaft):  $\alpha,\beta$ -unsaturated polyester diol having an OH number of 336 mg KOH/g, an acid number of 0.7 and a molecular weight factor per double bond of

262, prepared by polycondensation of maleic anhydride, 1,3-propanediol and diethylene glycol in a molar ratio of 1:1:1.

### Example 2

5

Production of a flexible polyurethane foam which was employed as a model for standard flexible foams by mixing 750 g of A component with 349 g of B component (index: 90) and transferring the foaming mixture into an aluminum mold (40 x 40 x 10 cm)

10 heated to 53°C; the components had the following compositions:

#### A component

97 parts of a polyol having an OHN of 28 mg KOH/g, a mean  
15 functionality of 2.3 and an EO/PO ratio of 14/86,

3 parts of a polyol having an OHN of 42 mg KOH/g, a mean functionality of 3 and a PO/EO ratio of 30/70,

20 3.31 parts of water,  
0.22 part of 1,4-diazabicyclo[2.2.2]octane,  
0.14 part of Lupragen® N 206 (BASF Aktiengesellschaft),  
0.5 part of Tegostab B 8631 (Goldschmidt).

#### 25 B component

Mixture of 50% of a polymeric MDI and 50% of a bifunctional MDI mixture.

30 Table 2: Comparison of the MDA contents of flexible PUR foams without (foam 9) and with addition of  $\alpha,\beta$ -unsaturated carbonyl compounds (foams 10 and 11)

Foam	9	10	11
35 Hydroxyethyl acrylate [% by weight to (A)]	-	10	
Laromer® 8765 [% by weight to (A)]	-	-	10
Cream time[s]	13	15	-
Gel time [s]	45	70	-
40 Rise time [s]	80	-	-
4,4'-MDA [ppm] w.o.a.	<1	<1	<1
2,4'-MDA [ppm] w.o.a.	<1	<1	<1
4,4'-MDA [ppm] w.a.	32	20	25
45 2,4'-MDA [ppm] w.a.	78	57	64

(A): Addition of (i) to the polyol component

(B): Addition of (i) to the isocyanate component

w.o.a.: Extraction after processing of the foam

w.a.: Extraction after hot-humid ageing for 3 days at 90°C and 90% relative atmospheric humidity in an air-conditioned chamber

### 5 Example 3

Production of a flexible polyurethane foam by mixing 750 g of A component with 275 g of B component (index: 115) and transferring the foaming mixture to an open mold having a volume of 40 l; the 10 components have the following compositions:

#### A component

100 parts of Lupranol® 2080 (BASF),

15 2.65 parts of water,

0.25 part of Lupragen® N 101 (BASF),

0.04 part of Lupragen® N 206 (BASF),

0.20 part of tin dioctoate,

0.80 part of silicone stabilizer BF 2370

20

#### B component

Lupranat® T 80 (BASF)

25 Table 3: Comparison of the TDA contents of flexible PUR foams without (foam 12) and with addition of  $\alpha,\beta$ -unsaturated carbonyl compounds (foams 13 to 16)

30	Foam	12	13	14	15	16
	Hydroxyethyl acrylate [% by weight to (A)]	-	5	-	-	-
	3-(Acryloyloxy)-2-hydroxypropyl methacrylate [% by weight to (A)]	-	-	5	-	-
35	Laromer® 8765 (BASF AG) [% by weight to A]	-	-	-	10	-
	Lupragen® VP 9198 (BASF AG) [% by weight to A]	-	-	-	-	10
40	2,4-TDA [ppm] w.o.a.	<1	<1	<1	<1	<1
	2,6-TDA [ppm] w.o.a.	<1	<1	<1	<1	<1
	2,4-TDA [ppm] w.a.	31	10	7	9	3
	2,6-TDA [ppm] w.a.	8	6	4	5	2

45 (A): Addition of (i) to the polyol component

(B): Addition of (i) to the isocyanate component

w.o.a.: Extraction after processing of the foam

w.a.: Extraction after hot-humid ageing for 3 days at 90°C and 90% relative atmospheric humidity in an air-conditioned chamber

The detection limit of the capillary electrophoretic  
5 determination is 1 ppm.

The advantages obtained according to the present invention, i.e.  
the significantly lower content of primary aromatic amines after  
ageing under hot and humid conditions, could thus be convincingly  
10 demonstrated.

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